Facile Synthesis of SnO₂ Nanorods for Na-Ion Batteries

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Nanostructure is attractive and has been proved superior in numerous applications due to the unique physical and chemical properties of the nano-materials. However, facile preparation of the nanostructured materials remains challenging; much effort is still essential to obtain materials with designed morphology. As a semiconductor, SnO₂ has been found a variety of applications such as solar cells and sensors, and has been extensively investigated as an anode material for lithium (Li)-ion batteries. Herein, we present a one-step and eco-friendly method to synthesize SnO₂ nanorods without any templates or additives. On the basis of its structural and morphologic evolutions probed by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), SnO₂ nanoparticles are proposed to firstly form from its precursor Na₂SnO₃·3H₂O and then assembled to nanorods with increased hydrothermal reaction time. When used as an active material for sodium (Na)-ion batteries, the as-prepared SnO₂ nanorods show a high Na-storage capacity and initial coulombic efficiency as well as good cycling stability. Our findings shed light on the preparation of nanostructured materials and contribute to developing high-performance Na-ion batteries.

Keywords: Nanostructured; SnO₂; Nanorods; Na-ion batteries

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Introduction

Nanostructured materials have shown many great advantages in various applications, owing to their distinctive physical and chemical properties.¹⁻³ A variety of nanostructures have been developed, including nanoparticles,^{4, 5} nanorods,^{6, 7} nanotubes^{8, 9} and nanobelts,¹⁰ nanosheets,¹¹ and hollow spheres,¹² *etc.* Among these nanostructures, one-dimensional (1D) nanorods demonstrate excellent performances in electronic and photonic devices due to their specific properties along the axial or in the radial directions.^{13, 14} However, templates or additives usually have to be employed during the preparation,¹⁵ making the fabrication complicated and the commercialization difficult. Therefore, it is essential to develop new facile synthesis methods.

As a semiconductor, SnO₂ has been widely applied in solar cells,¹⁶ gas sensors,¹⁷ catalysts,¹⁸ microwave absorption,¹⁹⁻²³ *etc.* It is also a promising anode material for lithium-ion (Li-ion) batteries due to its high Li-storage capacity (780 mAh g⁻¹), low-toxicity and high abundance.²⁴ Its electrochemical performances in sodium (Na)-ion batteries, however, are still far from satisfactory due to its low electric conductivity and large volume changes during cycling^{25, 26}. Nanostructures are expected to mitigate these issues by shortening the diffusion lengths of the ions and alleviating the volume change during cycling.²⁷⁻²⁹ Li and

the coworkers³⁰ recently synthesized a hierarchical structure SnO₂/carbon composite via a hydrothermal reaction, which shows a high initial charge capacity of 633 mAh g⁻¹. By means of the freeze-drying method, Wang and the coworkers³¹ succeeded to anchor the SnO₂ nanocrystals on the sulfur/nitrogen co-doped graphene. Due to the bonding effect between the Sn²⁺ and the functionalized graphene, it displays an excellent rate performance for both the Li and Na ion batteries. Different from the SnO₂ nanocrystals, Wang and coworkers³² constructed a 1D SnO₂ nanorods/3D graphene aerogel composite through a novel chemical reduction-induced self-assembly process. With this unique structure, the composite exhibits a good storage performance and excellent rate performance.

Herein, we report a one-pot method for facile preparation of SnO₂ nanorods without any templates or additives. On the basis of the characterization on the structural and morphologic evolution, a formation mechanism of the SnO₂ nanorods was proposed. The high reversible Na-storage capacity and cycling stability proved the superiority of the SnO₂ nanorods as an anode material for Na-ion batteries. These findings shed light on the preparation of nanostructured materials and contribute to the development of Na-ion batteries.

Results and discussions

Fig. 1a shows the XRD patterns of the SnO₂ nanorods with different hydrothermal reaction time in the hybrid solvents (the corresponding samples are denoted as S-xH; xH stands for the reaction time). Phase-pure SnO₂ is obtained and all the diffraction peaks can be indexed to the tetragonal SnO₂ (JCPDS No. 41-1445). The broad peaks of S-0.5H at about 26.6°, 33.9° and 51.7° (2θ) demonstrate its low crystallinity. The increase of the reaction time from 0.5 h to 12 h results in enhanced crystallinity of SnO₂. Therefore, intensive diffraction peaks with a

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Fig. 1 Evolution of (a) XRD patterns and (b) Raman spectra of the SnO₂ with different hydrothermal reaction duration in the hybrid solvent. The SnO₂ obtained in deionized water (S(H₂O)-12) is shown for comparison.

Fig. 2 SEM images of SnO₂ nanorods prepared in water/ethanol hybrid media for different hydrothermal reaction times: a) 0.5 h, b) 1 h, c) 2 h, d) 12 h and side view (inset). The morphologies of the SnO₂ prepared with deionized water solvent for a hydrothermal treatment time of e) 2 h, f) 12 h are shown for comparison (inset for its magnified image).

narrow peak width are observed in the XRD pattern of S-12H.

The structural evolution of the SnO_2 nanorods is further characterized by Raman spectroscopy (Fig. 1b). The region of 400–900 cm^{-1} is usually used to determine the evolution of the crystallinity of SnO_2 .³³ The broad peak at about 576 cm^{-1} is ascribed to the nanostructured SnO_2 . As the reaction time increases to 2 h, new peaks appear at about 628 and 772 cm^{-1} , referred to the A_{1g} and B_{2g} modes of SnO_2 , respectively, corresponding to the stretching mode of Sn–O bonds.³⁴ These two peaks grow with increased reaction time and become dominant in S-12H. In this process, the intensity of the broad peak at 576 cm^{-1} fades. These indicate that the crystallinity of the SnO_2 nanorods is enhanced with increased reaction time, consistent with the above XRD results.

The evolution of the morphology of the SnO_2 nanorods is characterized by SEM (Fig. 2). The SnO_2 is firstly formed as nanoparticles on the Na_2SnO_3 slabs (Fig. 2a) and becomes angular after 1 h hydrothermal treatment (Fig. 2b). As the reaction time increases to 2 h, the shape of the nanorods becomes clear and the rods are well aligned. As the reaction time further increases to 12 h, only the nanorods of about 200 nm in length can be observed; they are regularly arranged to form an array (Fig. 2d). However, nano-spheres of about 200 nm in diameter are obtained when sole deionized water is used as

the solvent, with some nanorods on the surface of the nano-spheres (Figs. 2e and f).

Transmission electron microscopy (TEM) was employed to investigate the structure of the SnO_2 nanorods. As shown in Figure 3a, the as-prepared nanorods are uniform in size. The dotted ring-like selected area electron diffraction (SAED) pattern (inset in Fig. 3a) indicates the polycrystalline nature of SnO_2 . The diffraction rings from the inner to the outer are indexed to the (110), (101), (200), (211) and (310) planes of SnO_2 . Fig. 3b shows the HRTEM image of the SnO_2 nanorods. The spacing of the two adjacent lattice fringes is measured to be about 3.32 Å, corresponding to the (110) facet of SnO_2 . Therefore, the direction of growth of the nanorods is supposed to be along the [001] axis of SnO_2 , a characteristic of its anisotropic structures.^{13, 35}

A combination of the XRD, Raman, SEM, and TEM results suggests a possible formation mechanism of SnO_2 nanorods as schematically illustrated in Fig. 4. As the slab-like $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, a source for SnO_2 is gradually dissolved in the hybrid solvent, and SnO_2 is nucleated on the undissolved slab. The reaction can be expressed as³⁶

Fig. 3 The (a) TEM (inset for SAED pattern) and (b) HRTEM (inset for the magnified) images of the SnO_2 nanorods (sample S-12H).

Fig. 4 The schematic formation mechanism of the SnO_2 nanorods in the hybrid solvent.

The SnO_2 nanoparticles are then formed and assembled into nanorods along the [001] axis due to the higher surface energy of the (001) plane than that of the (110) plane.³⁵ When the reaction time is increased to 12 h, all the nanoparticles are assembled into nanorods.

The properties of the solvent for the hydrothermal reaction are critical for the morphology of SnO_2 . As Fig. 2 shows, although phase-pure SnO_2 can be obtained in H_2O (Fig. 1a), the SnO_2 nanoparticles aggregate to form spheres with some nanorods on the surface (Fig. 2f). On the other hand, the SnO_2 obtained from the pure $\text{C}_2\text{H}_5\text{OH}$ as the sole solvent has very poor crystallinity and irregular particle morphology. Uniform nanorods can only be produced in the hybrid solvent of H_2O and $\text{C}_2\text{H}_5\text{OH}$. Therefore, the presence of $\text{C}_2\text{H}_5\text{OH}$ in the hybrid solvent is essential as a structure-directing agent for the formation of nanorods and as a tailor of reaction rate for preventing the aggregation of the SnO_2 nanoparticles.³⁶

The as-prepared SnO_2 nanorods were used as the anode material for Na-ion batteries and cycled between 0.01 and 3.0 V vs. Na^+/Na at 10 mA g^{-1} (Fig. 5). The discharge slope between 0.30 V and 0.50 V is ascribed to the reduction of SnO_2 to Sn while the plateau at about 0.20 V is referred to the formation of the Na_xSn alloys ($0 < x < 3.75$).^{27, 37-39} The upper discharge potential slope disappears in the second cycle, confirming the irreversible reduction of SnO_2 .^{28, 40} The discharge and charge capacities of the SnO_2 nanorod are 622.2 and 218.4 mAh g^{-1} , respectively, and the coulombic efficiency is about 35.11 % in the first cycle. The low initial coulombic efficiency is attributed to the irreversible reduction of SnO_2 to Sn (the theoretical coulombic efficiency for the reactions, $\text{SnO}_2 + 4\text{Na}^+ + 4\text{e}^- \rightarrow \text{Sn} + 2\text{Na}_2\text{O}$, $\text{Sn} + 3.75\text{Na}^+ + 3.75\text{e}^- \leftrightarrow \text{Na}_{3.75}\text{Sn}$, is only 49.6 %) and the electrolyte decomposition.^{27, 29, 41} In the subsequent cycling, the coulombic efficiency increases to 95 %. The reversible capacity is stable and maintains at 300 mAh g^{-1} after 90 cycles (Fig. 5b), better than previously reported nanostructured SnO_2 .³⁸

Conclusions

In summary, phase-pure SnO_2 nanorods are prepared by a facile and eco-friendly method in a hybrid solvent without using any templates or additives. Characterization on the structural and morphologic evolution indicates that SnO_2 nanoparticles are firstly formed and then assembled

into nanorods with increased reaction time. Use of the hybrid solvent is critical for preventing aggregation of the SnO_2 nanoparticles and for forming uniform nanorods. As an anode material for the Na-ion batteries, the SnO_2 nanorods show a high Na-storage capacity. The electrochemical performances of the SnO_2 nanorods can be improved by, for example, increasing the conductivity of a SnO_2 -based composite. Considering the attractive nanostructure of the nanorods, this synthesis method is expected to find applications in preparing nanostructured materials for other fields, solar cells, sensors, and catalysts, for example.

Experimental section

Material preparation. All the chemicals were of analytical grade and used as received without any further purification. Typically, SnO_2 nanorods were prepared by hydrothermal treatment of 2 mmol L^{-1} sodium stannate ($\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, slab-like) in a hybrid solvent of 30 ml deionized water (H_2O) and 50 ml ethanol ($\text{C}_2\text{H}_5\text{OH}$) at 200 °C for 12 h. H_2O and $\text{C}_2\text{H}_5\text{OH}$ were also used as independent solvents to explore the effect of solvent on the structure and morphology of the obtained SnO_2 .

Structural characterization. The X-ray diffraction (XRD) signals were collected on an X'Pert Pro MPD X-ray diffractometer (D8 Advance with a LynxEye_XE detector, Bruker) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). The Raman spectra were recorded on a Renishaw Via-Reflex spectrometer (532 nm radiation) with a resolution of 2 cm^{-1} . The scanning electron microscopic (SEM) images were obtained on Hitachi S-4800 field-emission microscope. Transmission electron microscopic (TEM) images and selected area electron diffraction (SAED) patterns were captured on a Tecnai G2 F20 U-Twin field-emission microscope.

Electrochemical evaluation. The working electrode was prepared by casting slurry of the SnO_2 nanorods, multiwalled carbon nanotubes (XF Nano; 10-20 nm in internal radius and 10-30 μm in length) and sodium alginate in deionized water at a weight ratio of 60:20:20 on a clean aluminum (Al) current collector. In an Ar-filled glove box, button-type test cells were assembled with Na foil as the counter electrode, glass fiber as the separator and 1.0 mol L^{-1} NaClO_4 dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (4:6 in volume) as the electrolyte. The electrochemical performances of the SnO_2 nanorods were evaluated on a Land BT2000 battery tester (Wuhan, China) at room temperature.

Fig. 5 (a) Selected potential profiles of the SnO_2 nanorod between 0.01 and 3.0 V vs. Na^+/Na and (b) its cycling performances (specific capacity and coulombic efficiency).

Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

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No competing financial interests have been declared.

Notes

Any additional relevant notes should be placed here.

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Abbreviations

XRD, X-ray diffraction; SEM, scanning electron microscopy; TEM, transmission electron microscopy; Li-ion, lithium-ion; Na-ion, sodium-ion; SAED, selected area electron diffraction; EC, ethylene carbonate; DEC, diethyl carbonate

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